DUAL CURE LOW-VOC COATING PROCESS

Phase III

Semi-Annual Technical Progress Report

For the Period April 1 - September 30, 1992

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**Industrial Gaseous Waste Reduction —
Phase III**

Semi-Annual Technical Progress Report

for the period April 1 – September 30, 1992

Issued: September, 1993

This Semi-Annual Technical Report has been prepared by Mr. Kevin E. Kinzer
for Contract No. DE-AC04-88ID12692 modification A007 with the Department of
Energy

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**SEMI-ANNUAL REPORT
DOE CONTRACT DE-AC04-88ID12692
INDUSTRIAL GASEOUS WASTE - PHASE III**

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SUMMARY

The objective of Phase III of 3M's contract with the U.S. Department of Energy is to complete proof-of-principle testing in full-scale systems of the dual cure photocatalyst technology developed in earlier Phases of the program. The Phase III commercial applications to be demonstrated are aerospace topcoats, aerospace primers, and solventless manufacture of tape backings.

In the second six months of Phase III, work has continued in all three applications. Significant progress has been made in improving the performance of the urethane/acrylate formulation being used for the aerospace topcoat application. Key improvements have been made in obtaining increased reverse impact, initial gloss and gloss retention during accelerated weathering. Technical challenges have continued with the aerospace primer formulation. Efforts in this six months have continued to focus on establishing a good baseline epoxy/acrylate formulation with reliable cure conditions. Work on the third demonstration application, development of solventless backing saturants for electrical tape backings, has essentially been completed. Optimal dual cure resin formulations have been identified and utilized in preparing complete tape constructions. These tapes have been evaluated and characterized in terms of benchmark UL and internal 3M specifications for electrical tape performance.

TASK 1: DEVELOP DUAL CURE URETHANE/ACRYLATE AEROSPACE COATINGS

The goal of this task is to develop a dual cure urethane/acrylate aerospace coating which meets the performance requirements of existing solvent borne urethane topcoats. Current materials are qualified under one of three specifications: MIL-C-83286 "Aliphatic Isocyanate Urethane Coating for Aerospace Applications" for low solids solvent based urethanes, MIL-C-85285 "High Solids Polyurethanes", or Boeing Material Specification (BMS) 10-60 "Protective Enamel" for commercial aircraft topcoats. The key requirements for each of these specifications are summarized in Appendix 1. Four sub-tasks were proposed for the urethane/acrylate coating task. First, to select and prepare suitable substrates for testing. Second, to optimize and screen coating formulations using a series of tests selected from the qualification standards. Third, to perform testing at 3M and Boeing Defense and Space Group of selected formulations using a wider range of the qualification tests. Fourth, to determine and optimize application and cure techniques for the dual cure urethane/acrylate compositions. The screening tests identified for sub-tasks two and three are summarized in Appendix 2. While these four sub-tasks were proposed to run sequentially, there has been considerable overlap between the individual tasks, especially sub-tasks 1.2 and 1.3 which call for the screening and optimization of topcoat formulations and qualification testing of these formulations. At the end of the first six months of the Phase III contract, substrate preparation had been completed, a formulation had been developed which largely met the screening requirements, and the second stage of qualification testing, including accelerated weathering, had been started. The efforts in this second six month period have focused on improving gloss and accelerated weathering performance of the coating while maintaining the performance level of the other screening criteria.

Sub-task 1.1: Select and Prepare Substrates

This sub-task was completed and reported on at the end of the first six months of the Phase III contract.

Sub-task 1.2: Optimize and Screen Coating Formulations

By the end of the first six months of Phase III a baseline formulation had been developed which was meeting the screening criteria of pencil hardness, impact flexibility, cold temperature bending as well as 7 and 30 day Skydrol resistance. However, this baseline formulation was not meeting the initial 60 degree gloss criteria and no accelerated weathering results were available at the end of the first six months. Furthermore, a strong relationship between gloss and pigment loading had been demonstrated during this first six months. The formulation in use at the end of the first six months of Phase III is shown below.

35%	Pigment (TiO ₂)
65%	Resin, consisting of
	70% Urethane Precursors

	Polyol 2
	Isocyanate 1
	30% Acrylates
	70% Monoacrylate 1 or Monoacrylate 2
	30% Diacrylate 1 or Diacrylate 4
0.25%	Iron photocatalyst (CpFeXylPF ₆) (on total resin wt.)
0.7%	Dispersant 1 (2% on pigment)
0.4%	Co-catalyst 1 (2% of acrylate resin)
1.0%	Oxygen Scavenger 2 (5% of acrylate resin)

The efforts in this second six month period have focused on improving gloss and accelerated weathering performance of the coating while maintaining the performance level of the other screening criteria.

The four possible acrylate combinations for the baseline formulation were prepared and knife coated on panels for 500 hour salt spray and accelerated weathering tests. All of the formulations were based on the same 70:30 urethane to acrylate ratio, 35% pigment loading, and identical urethane resins and catalyst system. See Table 1.1.

Table 1.1: Effect of various acrylate combinations on salt spray and Xenon accelerated weathering. All samples contain 35% pigment, Polyol 2, Isocyanate 1, 0.25% iron photocatalyst, 2% Dispersant 1, 2% Co-catalyst 1 and 5% Oxygen Scavenger 2 and a 70/30 ratio of monoacrylate/diacrylate.

Acrylate	500 hr. Salt Spray	Initial Gloss	261 hr. Gloss	514 hr. Gloss
Mono1/Di4	pass	80	38	9
Mono2/Di4	pass	79	35	8
Mono1/Di1	pass	80	31	8
Mono2/Di1	pass	80	39	10

All four acrylate combinations in the baseline formulation passed the 500 hour salt spray requirement. However, at 500 hours of accelerated weathering in the Xenon weatherometer, all samples showed a significant decrease in gloss to levels below 10%. This type of behavior was not observed with clearcoat urethane/acrylate formulations subject to Xenon weatherometer during Phase II.

Due to the poor results of the initial formulations described in Table 1.1, efforts were focused on identifying means of improving the accelerated weathering performance of these pigmented urethane/acrylate coatings. The four possible acrylate combinations for the baseline formulation were prepared with the addition of 0.6% UV Absorber 1, 1.8% Light Stabilizer 1 and 1.2% Light Stabilizer 2. The samples were knife coated and submitted for accelerated weathering in the Xenon weatherometer. See Table 1.2.

Table 1.2: Effect of UV absorber/light stabilizer combination with various acrylate combinations on Xenon accelerated weathering. All samples contain 35% pigment, Polyol 2, Isocyanate 1, 0.25% iron photocatalyst, 2% Dispersant 1, 2% Co-catalyst 1 and 5% Oxygen Scavenger 2 and a 70/30 ratio of monoacrylate/diacrylate, along with 0.6% UV Absorber 1, 1.8% Light Stabilizer 1 and 1.2% Light Stabilizer 2.

Acrylate	Initial Gloss	242 hr. Gloss	504 hr. Gloss
Mono1/Di4	67	51	13
Mono2/Di4	64	49	13
Mono1/Di1	72	54	14
Mono2/Di1	70	56	19

The presence of the UV absorber/light stabilizer has two main effects. First, they reduce the initial gloss of the samples. Secondly, these additives appear to delay the rapid drop in gloss with accelerated weathering. However, the gloss after 500 hours is only slightly higher than those samples without these stabilizers.

The four possible acrylate combinations for the baseline formulation were evaluated at a reduced pigment loading of 25% TiO₂ by weight. The effect of reducing the pigment loading from 35% to 25% on gloss, reverse impact, and Skydrol resistance was determined. See Table 1.3.

Table 1.3: Effect of decreasing the pigment loading to 25% on gloss, pencil hardness, Skydrol resistance, and impact. All samples contain 25% pigment, Polyol 2, Isocyanate 1, 0.25% iron photocatalyst, 2% Dispersant 1, 2% Co-catalyst 1 and 5% Oxygen Scavenger 2 and a 70/30 ratio of monoacrylate/diacrylate.

Acrylate	Gloss	Initial Hardness	Hardness after 7 d Skydrol	Reverse Impact
Mono1/Di4	82.5	HB	HB	50
Mono2/Di4	83.5	F	HB	<40
Mono1/Di1	80	2H	HB	<40
Mono2/Di1	81	H	HB	<40

These results indicate a gloss improvement of 2-4% over the corresponding samples prepared at 35% pigment loading. No significant changes in the reverse impact or 7 day Skydrol tests were observed.

A sample was prepared using 80% Monoacrylate 2/20% Diacrylate 4, instead of the standard 70%/30% ratio, in an effort to improve the impact performance. See Table 1.4.

Table 1.4: Effect of varying the ratio of Monoacrylate 2/Diacrylate 4 on functional properties and VOC. All samples contain 25% pigment, Polyol 2, Isocyanate 1, 0.25% iron photocatalyst, 2% Dispersant 1, 2% Co-catalyst 1 and 5% Oxygen Scavenger 2.

Ratio of Mono2/Di4	Reverse Impact	Initial Hardness	Hardness after 7d Skydrol	Hardness after 30 d Skydrol	Gloss	VOC
70/30	50	HB	HB	HB	81	4.2
80/20	60	F	4B(fail)	--	80	4.4

The 80/20 sample demonstrated an improvement in impact from 50 to 60 in-lbs., comparable VOC level to the corresponding standard formulation, and a 1% reduction in 60 degree gloss. However, poor Skydrol resistance was observed.

Formulations containing an allyl ether in place of some of the acrylate phase were prepared. This material acts as both a monomer and an oxygen scavenger. Good cure, VOC level, and gloss was obtained; however, the samples yellowed when placed in an oven. Hence, no further evaluations were conducted on this material.

In an attempt to isolate the cause of the poor weathering performance, the following pigmented samples were prepared: pure urethane; urethane plus Co-catalyst 1; urethane plus Co-catalyst 1 and Oxygen Scavenger 2; and the four urethane/acrylate combinations without Oxygen Scavenger 2. Initial gloss was measured and the samples were subjected to 245 hours in the Xenon weatherometer chamber. See Table 1.5.

Table 1.5: Xenon accelerated weathering results for pigmented samples prepared with various combinations of the baseline formulation.

Sample	Initial Gloss	245 hr. Gloss
pure urethane (Polyol 2/Isocyanate1)	84	12
pure urethane with Co-catalyst 1	84	9
pure urethane with Co-cat 1 & O ₂ Scav. 2	86	7
urethane/acrylate (Mono1/Di4)	78	12
urethane/acrylate (Mono2/Di4)	80	10
urethane/acrylate (Mono1/Di1)	77	14
urethane/acrylate (Mono2/Di1)	82	10

The gloss of all of the samples decreased rapidly in accelerated weathering. Based on these results, Polyol 1 was determined to be the primary cause of the poor weathering behavior. Work began on trying to identify a replacement for Polyol 1 which would result in improved weathering while maintaining the other performance properties.

In an attempt to identify a replacement for Polyol 1 in order to improve weathering, nine sets of pure urethane (no acrylate) samples were prepared based on different Polyols and Polyol blends containing 35% TiO₂. Samples were made for accelerated weathering, Skydrol resistance, and reverse impact testing. See Tables 1.6 and 1.7.

Table 1.6: Effect of Polyol in pure urethane pigmented formulations on functional properties. All samples contain 35% pigment.

Polyol	Initial Hardness	Hardness after 7 d Skydrol	Hardness after 30 d Skydrol	Reverse Impact
Polyol 2	2H	F	HB	70
Polyol 3	2H	2B	4B	>100
3:1 Polyol 2/3	2H	F	B	110
Polyol 4	2H	<6B	<6B	>120
Polyol 5	F	B	B	70
Polyol 1	4H	4H	5H	70
1:1 Polyol 1/3	2H	F	B	70
1:3 Polyol 1/3	2H	B	B	>120
3:1 Polyol 1/3	2H	2H	2H	80

Table 1.7: Effect of Polyol in pure urethane pigmented formulations on Xenon accelerated weathering. All samples contain 35% pigment.

Polyol	Initial Gloss	250 hr. Gloss	500 hr. Gloss
Polyol 2	85	22	7
Polyol 3	88	54	37
3:1 Polyol 2/3	85	35	14
Polyol 4	89	53	37
Polyol 5	83	14	18
Polyol 1	86	75	33
1:1 Polyol 1/3	88	68	37
1:3 Polyol 1/3	88	58	36
3:1 Polyol 1/3	88	75	36

Transmission electron micrographs were received from the 3M Corporate Analytical Laboratory. These evaluations indicate phase separation is not likely to be the cause of poor gloss. All phases appear to be less than 0.1 micron in size. Cross-sectional views show a loss of acrylate near the surface of the film sample. This supports the theory that gloss reduction is due to acrylate loss caused by surface oxygen inhibition. This inhibition results in poorer acrylate cure in the topmost layer of the film, resulting in film shrinkage and/or TiO₂ concentrating at the surface which reduces gloss.

Four different isocyanates were examined as possible replacements to the current material. The objective was to obtain faster urethane cure to retain acrylate at the film

surface. All four alternatives provided higher VOC levels and longer tack-free cure time than the standard. There appears to be a negative correlation between isocyanate viscosity and VOC level. See Table 1.8.

Table 1.8: Effect of Isocyanate type and viscosity on the VOC level. All samples contain Polyol 2, Monoacrylate 1, Diacrylate 1, and no Oxygen Scavenger.

Isocyanate	Viscosity (cP)	VOC (% of resin)
Isocyanate 1	600	15.8
Isocyanate 2	550	19.7
Isocyanate 3	550	18.6
Isocyanate 4	460	20.9
Isocyanate 5	280	23.3

A series of Light Stabilizers were evaluated for their effect on VOC and pot life. Some of these materials resulted in significant shortening of pot life; however, several materials were identified which do not appear to strongly affect pot life. Several of these additives were incorporated into urethane/acrylate formulations and examined for their effect on accelerated weathering. The results from these evaluations are reported later in this section.

Based on the results of the tests on the pure urethane formulations, two Polyol blends, Polyol 1 with Polyol 3 and Polyol 1 with Polyol 4, were selected for further evaluation as part of a complete pigmented urethane/acrylate composition. Five samples containing Polyol 1 with Polyol 4 in varying ratios and three samples containing Polyol 1 with Polyol 3 in varying ratios were prepared for reverse impact, Skydrol resistance, and accelerated weathering evaluations. Each sample also contained 35% pigment and the standard 70/30 ratio of urethane to acrylate. The acrylate used was a mixture of monoacrylate 2 and diacrylate 4. These samples were knife coated on BMS 10-11 primed panels. See Tables 1.9 and 1.10.

Table 1.9: Effect of Polyol blend on functional properties. All samples contain 35% pigment, Isocyanate 1, 70/30 ratio of Monoacrylate 2/Diacrylate 4, 0.25% iron photocatalyst, 2% Dispersant 1, 2% Co-catalyst 1 and 5% Oxygen Scavenger 2.

Polyol Blend	Reverse Impact	Initial Hardness	Hardness after 7 d Skydrol	Hardness after 30 d Skydrol
100% Polyol 1	45	HB	B	<6B
95/5 Polyol 1/4	30-35	B	B	<6B
90/10 Polyol 1/4	45	F	B	2B
80/20 Polyol 1/4	45	F	2B	4B
70/30 Polyol 1/4	60	H	B	<6B
70/30 Polyol 1/3	60	HB	2B	<6B
65/35 Polyol 1/3	65	B	3B	<6B
60/40 Polyol 1/3	>80	B	3B	<6B

Table 1.10: Effect of Polyol blend on Xenon accelerated weathering. All samples contain 35% pigment, Isocyanate 1, 70/30 ratio of Monoacrylate 2/Diacrylate 4, 0.25% iron photocatalyst, 2% Dispersant 1, 2% Co-catalyst 1 and 5% Oxygen Scavenger 2.

Polyol Blend	Initial Gloss	250 hr. Gloss	500 hr. Gloss
100% Polyol1	78	67	36
95/5 Polyol 1/4	77	67	33
90/10 Polyol 1/4	79	63	28
80/20 Polyol 1/4	77	62	29
70/30 Polyol 1/4	79	58	25
70/30 Polyol 1/3	77	53	22
65/35 Polyol 1/3	78	51	23
60/40 Polyol 1/3	76	47	22

These samples demonstrate better accelerated weathering performance than those formulations containing Polyol 2. However, all except one sample failed the 30 day Skydrol resistance requirement. The pigment in these samples was not milled. The poor Skydrol performance is suspected to be the result of poor dispersion of the pigment in the samples. The 70/30 Polyol 1/3 blend was identified as a candidate for further evaluations.

A series of auxiliary compounds to accelerate the catalyst activity were examined in an attempt to improve the surface cure of the urethane/acrylate formulations and hence improve the gloss. The effect of different Accelerants at various concentrations was determined by measuring the effect on gloss, yellow index (b^*), and VOC. See Table 1.11.

Table 1.11: Effect of type of Accelerant and concentration on gloss, yellowness and VOC level. All samples contain 35% pigment, Isocyanate 1, Polyol 2, 70/30 ratio of Monoacrylate 2/Diacrylate 4, 0.25% iron photocatalyst, 2% Dispersant 1, 2% Co-catalyst 1 and 5% Oxygen Scavenger 2.

Accelerant	Accelerant Concentration	Gloss	Yellow Index (b*)	VOC
Control	none	76	3.9	4.4
Accelerant 1	0.5%	74	4.3	4.9
Accelerant 2	0.5%	90	14.1	4.8
Accelerant 3	0.5%	87.5	6.8	4.9
Accelerant 4	0.05%	74	3.9	3.6
Accelerant 4	0.1%	76.5	4.2	3.8
Accelerant 4	0.25%	85	4.9	2.3
Accelerant 4	0.5%	88.5	6.5	4.4
Accelerant 5	0.5%	90	7.8	3.9
Accelerant 6	0.55%	89	7.9	3.9
Accelerant 7	0.55%	81.5	4.5	5.4
Accelerant 8	0.55%	81.5	4.5	4.7
Accelerant 9	0.55%	74	4.1	4.1
Accelerant 10	0.25%	79	---	4.5
Accelerant 10	0.5%	85.5	---	4.8

These Accelerants were found to result in significantly improved initial gloss values. However, in most cases addition of an Accelerant caused some discoloration. The Accelerants appeared to have negligible effect on the VOC value. Accelerant 10 was identified as a candidate for further evaluation since it seemed to represent the best compromise between initial gloss and discoloration. Minimum yellowing was observed in these samples. Additional samples were prepared with Accelerant 10 at various concentrations. The effect of Accelerant 10 concentration on initial gloss is shown in Table 1.12.

Table 1.12: Effect of Accelerant 10 concentration on initial gloss. All samples contain 35% pigment, Isocyanate 1, Polyol 2, 70/30 ratio of Monoacrylate 2/Diacrylate 4, 0.25% iron photocatalyst, 2% Dispersant 1, 2% Co-catalyst 1 and 5% Oxygen Scavenger 2.

Accelerant 10 Concentration	Gloss
0% (control)	78
0.34%	87
0.42%	88
0.5%	88.5
0.64%	92
0.75%	92
1.0%	92

Dispersant screening was conducted in an attempt to determine the best Dispersant type and concentration for use with the 70/30 Polyol 1/3 blend. The optimum concentration of each Dispersant was determined by identifying the point at which the viscosity of the mill base reached a minimum. The pencil hardness, Skydrol resistance and impact performance of samples containing various Dispersants at optimal concentrations is shown in Table 1.13.

Table 1.13: Effect of Dispersant type on pencil hardness, Skydrol resistance, and reverse impact of samples containing 70/30 Polyol 1/3 blend.

Dispersant	Initial Hardness	Hardness after 7 d Skydrol	Reverse Impact
Dispersant 3	2H	<6B	60
Dispersant 6	H	<6B	50
Dispersant 1	2H	2H	70

Based on these evaluations Dispersant 1 was identified as the best Dispersant type for use with this Polyol blend.

A mill base was prepared using Dispersant 1 with the 70/30 ratio of Polyol 1 to Polyol 3 blend. Ten samples plus a control were prepared and submitted for Xenon accelerated weathering testing. All of the samples contained 35% pigment, the 70/30 ratio of monoacrylate 2 to diacrylate 4 with various UV light absorbers/light stabilizer combinations and with several of the Accelerants which looked promising based on improved initial gloss. The composition of the samples submitted for accelerated weathering is shown in Table 1.14.

Table 1.14: Weathering additives and Accelerants in the samples submitted for Xenon accelerated weathering. All samples contain 35% pigment, 70/30 Polyol 1/3, Isocyanate 1, 70/30 Monoacrylate 2/Diacrylate 4, Dispersant 1, and Oxygen Scavenger 2

Sample	UV Absorber	Light Stabilizer	Accelerant
control	none	none	none
1	1% UV Absorb. 2	1% Light Stab. 3	none
2	1.6% UV Absorb. 3	0.4% Light Stab. 3	none
3	1% UV Absorb. 4	1% Light Stab. 3	none
4	1% UV Absorb. 2	1% Light Stab. 4	none
5	1.6% UV Absorb. 3	0.4% Light Stab. 4	none
6	1% UV Absorb. 4	1% Light Stab. 4	none
7	none	none	0.5% Accel. 10
8	none	none	0.5% Accel. 7
9	none	none	0.5% Accel. 8
10	none	1% LS 3+1% LS 4	none

Sub-Task 1.3: Qualification Test Selected Formulations

Due to the considerable overlap between sub-tasks 1.2 and 1.3 and the need to perform the work simultaneously, the majority of the results from both sub-tasks are reported above under sub-task 1.2.

Two one quart kits of a pigmented topcoat formulation were prepared, along with Material Safety Data Sheets, and samples to Boeing Defense and Space Group. These two samples had identical resin formulations, but differed in the pigment loading. The two loadings were 25% and 35%. Samples were sprayed using several different solvents or solvent mixtures to provide enough thinning to achieve a sprayable viscosity. These initial tests indicated that a pigment loading of greater than 25% was required to obtain acceptable hide with a 2 mil coating.

By the end of the second six month report period, even though not all of the screening criteria had been met, considerable progress had been made in developing formulations which demonstrate improved initial gloss and accelerated weathering performance over the baseline formulation which was reported at the end of the first six month report period. The new baseline topcoat formulation is shown below.

35%	Pigment (TiO ₂)
65%	Resin, consisting of
	70% Urethane Precursors
	70:30 ratio of Polyol 1 & Polyol 3
	Isocyanate 1
	30% Acrylates
	70% Monoacrylate 2
	30% Diacrylate 4
0.25%	Iron photocatalyst (CpFeXylPF ₆) (on total resin wt.)
0.7%	Dispersant 1 (2% on pigment)
0.4%	Co-catalyst 1 (2% of acrylate resin)
1.0%	Oxygen Scavenger 2 (5% of acrylate resin)
	Weathering Additives
	Accelerant

As of the end of this reporting period, samples containing the above formulation with various promising Weathering Additives and Accelerants had been prepared. No test results were yet available on the samples.

Sub-task 1.4: Determine and Optimize Application and Cure Techniques

Virtually all formulation experiments performed under sub-tasks 1.2 and 1.3 were performed using knife coated test panels due to the convenience of this technique for routine evaluations in the laboratory. In an attempt to remove one additional source of potential variability, most formulation experiments were performed using the same cure conditions: 15 minute solvent flash period followed by 15 minute exposure at a given lamp to sample distance under super actinic lights at room temperature.

An experiment was conducted to assess the effect of lamp to sample distance, hence lamp intensity, on the cure and VOC. Reduction of the lamp intensity from 100% of normal to 80%, 60% and 40% of the normal illumination resulted in no significant effect on cure and minimal effect on the VOC level. Some gloss improvement was noted as the lamp intensity was decreased.

Initial spray experiments were done at Boeing using 25% and 35% pigmented urethane/acrylate topcoats. The results from these trials indicated that 35% TiO₂ was needed for hide, 25% pigment samples did not hide adequately. During these spray trials a limited selection of solvents was evaluated.

TASK 2: DEVELOP DUAL CURE EPOXY/ACRYLATE AEROSPACE PRIMERS

The goal of this task is to develop a dual cure epoxy/acrylate aerospace coating which meets the performance requirements of existing solvent borne epoxy primers. Current materials are qualified under one of three specifications: MIL-P-23377 "Primer Coatings: Epoxy, Chemical and Solvent Resistant" for conventional hydrocarbon solvent coatings; MIL-P-85582 "Primer Coatings: Epoxy, Waterborne"; or Boeing Materials Specification (BMS) 10-79 "Urethane Compatible Corrosion Resistant Primer" for commercial aircraft primers. The key requirements for each of these specifications are summarized in Appendix 3. Four sub-tasks were proposed for the epoxy/acrylate coating task, which parallel task 1 in organization. However, Boeing Defense and Space Group is not a partner in the task 2 testing. First, to select and prepare suitable substrates for testing. Second, to optimize and screen coating formulations using a series of tests selected from the various qualification standards. Third, to perform testing of selected formulations using a wider range of the qualification standards. Fourth, to determine and optimize application and cure techniques for the dual cure epoxy/acrylate compositions. The substrate preparation is complete; however, work on screening epoxy/acrylate formulations is behind forecast due to technical problems overcoming inhibition to cure due to moisture and emphasis on the topcoat development.

Sub-task 2.1: Select and Prepare Substrates

This sub-task was completed and reported on at the end of the first six months of the Phase III contract.

Sub-task 2.2: Optimize and Screen Coating Formulations

During the first six months of the Phase III contract a series of screening tests were identified for performing initial evaluations of primers relative to the military and commercial specifications. These test were selected to allow rapid assessment of coating performance and evaluation of the impact of formulation changes. The screening test proposed were: pencil hardness, wet and dry tape adhesion, impact flexibility, cold temperature bending, hydraulic fluid resistance, distilled water

resistance, salt spray resistance, and filiform corrosion. In addition to these tests, VOC levels are routinely measured to assure that adequate cure is being achieved.

During the first six months a baseline formulation was identified. This formulation is shown below:

- 25% Chromate (BaCrO_4)
- 70% Resin, consisting of
 - 60% Epoxy 1
 - 40% Acrylates
 - 90% Monoacrylate 1
 - 10% Diacrylate 5
- 5% Pigment (TiO_2)
- 0.5% Iron Photocatalyst (CpFeXylSbF_6)
- 0.6% Dispersant 5 (2% of chromates + pigment)
- 0.6% Co-catalyst 1 (2% of acrylate resin)

This baseline formulation was not providing reliable cure. A range of filler types and levels had been examined, but no clear pattern was established. Surface effect of the filler, particularly silane treatment, appeared to have a positive effect on cure. However, at the end of the first six month report period, the problem of obtaining reliable cure for the epoxy/acrylate primer formulation remained largely unsolved. Formulations containing only chromate (at less than 10%), only pigment (TiO_2 , at less than 5%), or only filler appeared to cure well. However, formulations containing all of the these materials did not provide acceptable cure. Furthermore, coating viscosity was too low, giving rise to runs and sags on application. Attempts to increase the viscosity of formulations containing chromate and pigment, or chromate and kaolin by adding a thixatropes, were unsuccessful due to problems with air entrainment. The focus of effort in this reporting period has been on identifying and understanding the underlying cause of the unreliable cure in this system.

The effect of fillers on the cure of epoxy/acrylate formulations was examined. The effect of filler type and concentration on measured VOC level of samples cured for 15 minutes under super actinic bulbs is shown in Table 2.1.

Table 2.1: Effect of filler type and concentration on measured VOC (as % weight loss on resin).

Filler type	Filler concentration	% VOC on resin
none	none	5.0
Mica	5%	6.7
	10%	19.2
Talc	5%	5.1
	10%	5.3
	15%	8.2
	20%	16.0
Fumed Silica	0.5%	5.5
	1%	5.9
	2%	5.2
	3%	5.8
	5%	5.4
Silica Powder (granular)	5%	9.3
	10%	13.8
	15%	15.4
	20%	19.3
Barium Sulfate	8.7%	5.9
	17.4%	6.6
	26%	21.8
	34.7%	27.8
Chlorite	5%	6.7
	10%	6.8
	20%	22.4
	40%	28.5
Zeeospheres	30%	6.0

From these results, it can be seen that when added individually these fillers had the following effects on cure. Mica and granular silica were found to strongly interfere with the epoxy/acrylate cure. At 5% added mica, VOC levels increased approximately 1.7% and at 10% added mica, no cure was observed. Addition of talc provided good cure at the 10% level, but essentially no cure at loadings above 20%. Fumed silica could be added at levels up to 5% with good cure. Barium sulfate provided good cure up to approximately 18% and chlorite provided good cure up to 10%. Both of these fillers showed inhibition of epoxy cure at higher levels. Zeeospheres provide good cure up to at least 30%.

An evaluation of silane surface treatment on kaolin was previously identified and reported to significantly improve the cure of the epoxy/acrylate formulations. The effect of silane treatment on fumed silica and mica is shown in Table 2.2.

Table 2.2: Effect of silane treatment of fumed silica and mica on measured VOC (as % weight loss on resin).

Filler type	Silane treatment	Filler concentration	% VOC on resin
none			5.0
Fumed Silica	no	10%	13.9
	yes	10%	7.0
	no	20%	19.3
	yes	20%	10.1
Mica	no	5%	3.9
	yes	5%	3.9
	no	10%	13.8
	yes	10%	17.8
	no	15%	23.6
	yes	15%	25.0
	no	20%	30.6
	yes	20%	31.9

The silane treatment appears to have an advantageous effect on reducing the cure inhibition with fumed silica. However, no improvement is observed with silane treating mica. It was found that adding the silane to the pigment resin system, instead of pre-treating the filler with silane before dispersing it in the resin system, provided similar VOC levels as the pre-treated fillers.

The effect of TiO₂ type on epoxy/acrylate cure was evaluated and the results are presented in Table 2.3.

Table 2.3: Effect of TiO₂ type (at 10% loading level) on measured VOC (as % weight loss on resin).

TiO ₂ type	% VOC on resin
R-960	12.3
R-700	4.2
R-702	5.1
R-101	8.2
Kronos 2020	5.3

The current TiO₂ (R-960) being used is the same as the pigment in the urethane/acrylate topcoat formulation. This material is surface treated to provide better weathering performance, but it appears the surface treatment is negatively affecting epoxy cure. All four of the other TiO₂ pigments evaluated gave better epoxy cure.

A test was developed for detecting absorption of activated catalyst (free iron) on the surface of fillers using colorimetric indicators. Previous tests with silane surface

treated kaolin had shown good cure. Untreated kaolin was found to gel the epoxy/acrylate formulation. This was attributed to strongly acidic, active sites on the kaolin surface. Additional analytical experiments were conducted which demonstrated that the mechanism for cure inhibition by the various fillers was related to surface adsorption of the active catalyst. It was found that the use of silane treated fillers significantly reduced surface adsorption of the catalyst and therefore minimized the cure inhibition by the fillers.

Several experiments were conducted on epoxy/acrylate formulations with barium chromate and various fillers at different iron photocatalyst levels. The results are tabulated in Table 2.4.

Table 2.4: Effect of iron photocatalyst level on measured VOC level for epoxy/acrylate formulations with various fillers.

Fillers	Percent Photocatalyst	% VOC on Resin
10% barium chromate	0.5%	11.6
10% talc	1.0%	5.7
1% fumed silica		
20% barium chromate	1.0%	11.5
10% talc	1.5%	6.6
1% fumed silica	2.0%	5.9
20% barium chromate	0.5%	31
12% talc	1.0%	23.7
14% silica powder	1.5%	17.3
4% TiO ₂	2.0%	14.7

The amount of catalyst required to achieve good cure appears to be dependent on the amount and type of fillers in the formulation. At 10% barium chromate, 1.0% photocatalyst results in good cure. However, at 20% barium chromate, 1.5% photocatalyst is needed to achieve good cure. Higher filler loadings and the addition of pigment result in insufficient cure even at photocatalyst levels as high as 2.0%.

The effect of relative humidity and temperature on cure of the epoxy/acrylate primer formulation was evaluated by measuring tack free time and VOC level for clearcoat samples. A controlled temperature platen was constructed which allows for heating of test panels during cure. Samples were cured at room temperature (~22°C), 30°C and 40°C and relative humidity variations from 37 to 62%. The results are tabulated in Table 2.5. Acceptable cure rates were achieved at all temperatures evaluated at relative humidity below 50%. Tack free time ranged from 2.5 minutes to 60 minutes. However, acceptable cure rates could only be achieved by heating to 40°C when the relative humidity was above 50%.

Table 2.5: Effect of temperature and humidity on the cure rate of epoxy/acrylate clearcoat formulation.

Relative Humidity	Temperature (°C)	Tack Free Time (min)	% VOC on Resin
38%	22	35	4.8
38%	30	5	4.9
38%	40	2.5	5.9
48%	22	55	5.6
48%	30	9	4.7
48%	40	3	5.1
62%	22	no cure	18.6
62%	30	no cure	14.8
62%	40	16	7.7

TASK 3: DEVELOP SOLVENTLESS TAPE BACKING

The goal of this task is to evaluate the use of dual cure catalysts in saturating resins for tape backings. The properties of the dual cure catalyzed backings will be compared to the performance of similar, commercial materials using conventional solvent based technology. Five sub-tasks were proposed for the tape backing effort. First, to select a suitable tape backing substrate from a list of possible alternatives. Second, to determine the optimal resin formulation using laboratory scale experiments. Third, to establish optimal curing condition with the desired resin formulation. Fourth, to prepare samples of a completed pressure sensitive adhesive tape using the dual cure catalyzed backings. Fifth, to evaluate the properties of these experimental tapes compared to UL and internal 3M specifications for electrical tape performance.

Sub-Task 3.1: Select Tape Backing Substrates

Several substrates were saturated and evaluated for use as tape backings. Criteria used for selecting a backing included obtaining the proper adhesion between the saturating resin and the backing. The electrical and mechanical properties of the coated backing were also measured to determine the appropriate backing. The following substrates were saturated with UV curable epoxy solution:

- Polyester film
- Non-woven polyester film
- Glass cloth
- Cellulose acetate cloth
- Paper (crepe and flat back)

In the case of polyester films, different types of treated films were evaluated in order to obtain the proper adhesion between the epoxy and the backing. The five films chosen for this study were:

1. Unprimed film
2. Corona treated film
3. Primed film A
4. Primed film B
5. Primed film C

The films were coated and cured with epoxy solution and adhesion values were determined on these films. The adhesion values are reported in Table 3.1.

Table 3.1: Adhesion of dual cure epoxy to various Polyester films.

Polyester Film	Adhesion (Oz./inch)
Unprimed	2.8
Corona treated	Unable to separate
Primed film A	4.3
Primed film B	0.7
Primed film C	Unable to separate

Primed film C, which has been specially treated for epoxy adhesion, provided the best performance followed by the corona treated film. The coated backings were also post-cured at 120°C for 2,4,6 and 8 minutes and subsequently the adhesion values were determined. No increase in adhesion was observed as a result of a post-cure treatment.

The conclusion from this study was that the dual cure epoxy solution can be used with any backing needing a saturant to modify either the electrical or mechanical properties of the backing. In the case of polyester film, either Primed film C or corona treated film was needed to obtain adequate adhesion between the cured epoxy and the film.

Sub-task 3.2: Determine Resin Formulation

Several different formulation were prepared depending upon the application and the type of substrate used. The typical formulation contained the following:

- Base epoxy resin
- Flexibilizer
- Brominated epoxies (for flame retardancy)
- Pigments
- Fillers
- Flame retardant agents (antimony oxides)
- Iron photocatalyst (CpFeXylSbF₆)
- Co-catalyst

Different photocatalyst concentrations were evaluated in order to identify the amount needed to provide adequate cure in acceptable time periods. It was concluded that

1% photocatalyst was the optimum concentration for the conditions used in the laboratory (1% based on the weight of epoxy). The addition of the co-catalyst was also found to increase the curing rate and hence was used in all the formulations. The DSC (Differential Scanning Calorimeter) curves, shown in Figure 3.1, indicate the effect of the co-catalyst on the curing profile of one formulation.

The flexibilizers were used at different concentrations depending upon the backing and the desired amount of flexibility. The effect of flexibilizer concentration on physical properties of a saturated backing is shown in Table 3.2.

Table 3.2: Effect of flexibilizer concentration on physical properties of saturated tape backings. All samples contain Epoxy 1 and Flexibilizer 1.

Flexibilizer 1	Hardness (Shore D)	Tensile (psi)	Elong. (%)	Modulus (kpsi)	T _g (°C)
0%	84	5900	5	147	83
10%	83	5763	7	181	49
20%	79	3740	7	136	33
30%	71	1760	18	35	-4
40%	52	420	22	4.5	-20
50%	33	180	14	1.5	-24

Increasing the amount of flexibilizer resulted in increased flexibility (i.e. lower modulus and higher elongation) and reduced hardness and tensile strength. From the data in Table 3.2, it can be seen that the concentration of flexibilizer has a significant effect on the mechanical properties of the backing. This phenomenon can be utilized to vary the backing properties over a broad range of values. Formulations containing Flexibilizer 1 generally resulted in substrates with an odor. The backing was analyzed for the odor causing component but it was difficult to arrive at any conclusions from the analysis. Flexibilizer 2 produced backing with no odor and consequently was the preferred flexibilizer in most of the formulations.

Flame retardant formulations were prepared with Brominated epoxy and antimony oxides. To optimize the formulation, the effect of the ratio of the two flame retardant components on the flame test was studied. Samples with three different ratios of Br/Sb (the active flame retardant components) were prepared: 4.5, 3.0 and 1.15. UL-510 flame test was performed on the backings prepared from the above formulations containing the different ratios of the flame retardant additives. The results of the flame test are shown in Table 3.3.

Table 3.3: Effect of Br/Sb ratio on UL-510 flame test.

Br/Sb ratio	Average Flame Time
4.5	14 sec.
3.0	12 sec.
1.15	5 sec.

Figure 3.1: DSC thermogram of a tape-backing saturant system containing Epoxy 1 and Flexibilizer 1, with and without Co-catalyst 4.

There was some difference in the flame time for the three formulations, but all of the samples passed the UL-510 flame test, which specifies a 60 second maximum flame time. It was concluded that a ratio of 4.5 would be utilized since it contains the least amount of antimony trioxide.

Antimony pentoxide was also evaluated, since it is perceived to be a safer additive compared to antimony trioxide. Several formulations were prepared and cured with different levels of antimony pentoxide. Unfortunately the formulations containing antimony pentoxide did not seem to cure as rapidly as the antimony trioxide formulations. The impurities in antimony pentoxide (commercial sources contain only 55-65% antimony pentoxide) seem to hinder the curing mechanism of the iron photocatalyst. Therefore antimony trioxide was utilized in those formulations requiring flame retardancy.

The effect of the pigments on the formulations was also studied. Three different pigments were evaluated: black, yellow and white. The pigments were pre-dispersed in the epoxy and hence no problem with pigment dispersion was encountered. The backings were coated and cured with formulations containing the pigments. The pigments did not affect the cure and films of good quality were obtained from these formulations.

Sub-task 3.3: Establish Curing Conditions

The formulations prepared in our laboratory were coated and cured in a laboratory UV processor specially designed for this purpose. The flow diagram of this unit is shown in Figure 3.2. The unit consists of a coating station, UV curing unit and a winding station. The coating station can be modified to suit the coating operation without much difficulty. The UV processor is equipped with a variable intensity lamp with three different intensity settings. The winding station is controlled by a variable motor which controls the speed of the coating operation.

Several experiments were conducted to determine the optimum method of curing. Since the coating operations could be carried out at different speeds and different lamp intensities, an experiment was conducted which was designed to result in a backing which could be coated and fully cured as fast as possible. A glass cloth backing was coated and cured at 300 watts/inch intensity and three different speeds (4.6 ft/min., 9.7 ft/min. and 15.7 ft/min.). The samples were then characterized by DSC to determine the T_g (glass transition temperature) of the cured samples. There seems to be very little difference in the T_g values of the three different samples coated and cured at different speeds, indicating that all of the samples were cured to essentially the same degree. This indicates that the epoxy solution can be cured at high speeds without sacrificing the degree of cure.

To monitor the cure, a simple test was developed to determine the degree of cure. This test is based on wet chemistry utilizing a Bromophenol blue solution. This test was evaluated with several samples and seems to provide a qualitative indication of the degree of cure. This technique should prove to be useful as a quality assurance procedure in manufacturing.

UV PROCESSOR

Figure 3.2: Schematic of the laboratory UV Processor used in Sub-task 3.3.

The shelf-life of the formulation is an important criteria for production coating operations. Most of the current thermally cured epoxy solutions have a short shelf-life after the two parts have been mixed. One advantage of the UV cured epoxy solutions is the shelf-life that they have. Several sample formulations were stored and the viscosity monitored over a period of time. No appreciable change in viscosity was observed after approximately 9 months. Table 3.4 shows the viscosity versus time relationship for two formulations used in making tape backings.

Table 3.4: Shelf-life of epoxy formulations with and without Co-catalyst 4.

Time (days)	Viscosity (cP)	
	without Co-catalyst 4	with Co-catalyst 4
0	800	694
23	860	802
39	800	780
74	832	800
276	962	900

The effect of post-curing at elevated temperature on mechanical properties of the backing was also evaluated. Polyester film samples coated either one-side or both with an epoxy solution and cured on the laboratory UV processor were post-cured at 120°C in an oven for 2,4 and 6 minutes. Tensile and elongation were measured on the films and compared to a control film which was not post-cured. See Table 3.5. There was no noticeable change in the mechanical properties as the result of post-curing and hence it was concluded that no post-curing is necessary.

Table 3.5: Effect of post-curing at 120°C for various periods of time on film mechanical properties. All samples were coated with a 40/30/30 Epoxy 1/Brominated Epoxy/Flexibilizer 1 solution.

Sample	Post-Cure Time (min.)	Tensile (psi)	Elongation (%)
Control	none	50.1	140
1 side coated	0	60.4	92
1 side coated	2	53.4	84
1 side coated	4	53.4	84
1 side coated	6	53.4	88
2 side coated	2	48.7	122
2 side coated	4	49.0	125
2 side coated	6	49.5	135

The effect of coating thickness on the mechanical and electrical properties of the backing was studied. Two formulations were prepared and coated on a non-woven polyester backing. The coating orifice was varied from 4.5 to 8.0 mils. The cured backing was then characterized for tensile, elongation and dielectric strength. A coating orifice of 6 mils seems to give the proper balance of the properties. The backings were also post-cured at 100°C for 10 minutes and then tested for the above properties. The results of these experiments are shown in Tables 3.6 and 3.7.

Table 3.6: Effect of coating thickness on performance properties using a 40/30/30 Epoxy 1/Brominated Epoxy/Flexibilizer 2 formulation.

Wet Thickness (mils)	Cured Thickness (mils)	no post-cure			10 min., 220°F post-cure		
		Tensile (lb./in.)	Elongation (%)	Dielectric (kV)	Tensile (lb./in.)	Elongation (%)	Dielectric (kV)
4.5	3.8	30.3	27	1.3	30.7	20	2.8
5	4.2	31.7	29	3.3	35.8	24	3.5
6	4.4	30.4	32	5.5	33.0	22	6.3
7	5.1	28.9	34	6.1	37.2	25	6.5
8	6.0	32.7	29	4.8	40.6	26	6.0

Table 3.7: Effect of coating thickness on performance properties using a 50/30/20 Epoxy 1/Brominated Epoxy/Flexibilizer 2 formulation.

Wet Thickness (mils)	Cured Thickness (mils)	no post-cure			10 min., 220°F post-cure		
		Tensile (lb./in.)	Elongation (%)	Dielectric (kV)	Tensile (lb./in.)	Elongation (%)	Dielectric (kV)
4.5	4.2	31.3	21	1.6	29.2	15	2.6
5	4.2	34.1	28	5.2	31.7	18	4.7
6	4.6	35.2	28	5.5	31.3	13	5.6
7	5.3	25.7	27	5.8	34.6	17	6.6
8	5.8	34.1	26	6.6	39.1	19	6.9

Sub-task 3.4: Prepare Pressure Sensitive Adhesive Tape

Tapes were prepared by coating the saturated backings produced on the laboratory scale UV processor with one of two different adhesives. A rubber based adhesive was coated at a 3M pilot plant. An acrylic adhesive was coated by a transfer process and was done using small strips of the backing.

The first scale-up of the tape backing formulation was performed at the 3M Hartford City, Indiana plant in February of 1992. The epoxy solution was prepared in a large reactor producing about 1500 lbs. of the resin. About 4000 yards of polyester film and non-woven polyester film was coated at speeds ranging from 100 to 200 ft/min. with

four UV lamps. The polyester backing which was coated on both sides with the epoxy solution during this trial blocked upon sitting. The cause of this behavior was identified and can easily be avoided in the future. The experiments were highly successful and the simple process of coating and curing the epoxy solution was demonstrated.

A second scale-up experiment was conducted in St. Paul, Minnesota. Several coating methods were evaluated using epoxy solutions of different viscosities. Several different coating techniques were identified which can be used to coat these solutions at production speeds.

Sub-task 3.5: Evaluate Tape Properties

Several rolls of tapes produced in the laboratory were tested for standard tape properties and compared to the existing products. The results indicate that the performance of these tapes are quite similar to the standard tapes in most cases and should be accepted without any problem.

The following tests were performed on the tapes according to the 3M or ASTM specifications.

- Tensile
- Elongation
- Two Bond test
- Adhesion
- Dielectric Strength
- Flame Test (on flame retardant formulations)
- Insulation Resistance
- Electrolytic Corrosion
- Solvent Resistance

The effect of the flexibilizer on the final tape properties was studied. Four different formulations with varying amounts of the flexibilizer were prepared and cured. The backings were coated with a rubber based adhesive and in some cases with an acrylic adhesive. The rolls of tapes were then characterized and the results are reported in Tables 3.8 and 3.9.

Table 3.8: Backing properties produced from dual cure epoxy saturant with different concentration of Flexibilizer 1.

Backing	Epoxy 1 (parts)	Brominated Epoxy (parts)	Flexibilizer 1 (parts)	Thickness (mils)	UL-510 (secs)
A	40	30	30	5.2	<20
B	50	30	20	5.1	34
C	60	30	10	5.1	23
D	70	30	0	5.4	13

Table 3.9: Performance properties of tapes produced from dual cure backings saturated with different concentration of Flexibilizer 1 and coated with either rubber based or acrylic based adhesive.

Backing	Adhesive	Tensile (lb./in.)	Elong. (%)	2-bond (Oz/in)	Adhesion (Oz/in)	Dielectric (kV)	Resist. (ohms)
A	rubber	33	25	102	36	4.96	2.0E10
B	rubber	34	25	128	39	4.67	3.3E11
C	rubber	33	13	122	42	4.93	2.9E12
D	rubber	34	4	122	39	5.07	1.2E13
B	acrylic	34	26	97	45	5.70	
C	acrylic	33	14	88	45	4.26	

The physical and electrical properties of various backings coated with a rubber based adhesive were also measured and are reported in Tables 3.10 and 3.11.

Table 3.10: Physical performance properties of tapes produced from dual cure backings and rubber based adhesive along with control tape samples.

Backing	Formulation	Tensile (lb./in.)	Elongation (%)	Adhesion to Steel (Oz/in)	#2 Bond (Oz/in.)
Non-woven Polyester	50/30/20	34	7	26	96
	control	40	27	50	130
Flat-Back Paper	50/30/20	51	11	ruptured	106
	control	44	7	38	140
Crepe Paper	75/0/25	31	14	40	68
	control	24	10	27	98

Table 3.11: Electrical performance properties of tapes produced from dual cure backings and rubber based adhesive along with control tape samples.

Backing	Formulation	Insulation Resistance (Megaohm)	Electrolytic Corrosion	Dielectric Strength (Volts)
Non-woven Polyester	50/30/20	14.6×10^{14}	0.98	6280
	control	10.4×10^{14}	1.00	6640
Flat-Back Paper	50/30/20	$>10^{14}$	0.71	1800
	control	$>10^{14}$	0.72	2100
Crepe Paper	75/0/25	$>10^{14}$	0.78	2480
	control	9.0×10^{13}	0.63	2740

In most cases the properties of the tapes produced from dual cure backings are comparable to the control products currently being made by the solvent based process and the advantage of the UV process is the ease of the preparation of the backing. The control tapes which were tested for comparison purposes were made in the factory with much greater uniformity than the laboratory produced backings. The properties of the dual cure backings would be better when made in a factory process environment and compared to the standard products.

TASK 4: EVALUATE PROCESS PERFORMANCE

Based on the results obtained for each of the three demonstration applications, estimates of the energy savings, technical, and economic feasibility of the dual cure technology generated during Phases I and II of the DoE contract will be updated. No effort has been scheduled or occurred for task 4 during the second six months of the contract.

TASK 5: REPORTS, CONTRACT ADMINISTRATION, AND TECHNOLOGY TRANSFER

A DoE goal throughout the contract has been widespread exposure of the potential for the dual cure technology to provide substantial savings in energy usage and solvent consumption. This is accomplished via monthly reports to DoE, participation in external meetings and workshops, and presentations at various DoE sponsored meetings. During the second six months of the contract, a presentation on dual cure technology was made to DoE personnel in August 1992 at 3M Center in St. Paul, MN. A program review on the dual cure aerospace coatings program was made to Boeing and DoE personnel in July 1992 in Seattle, WA. 3M also participated in the DoE-OIT Waste Materials Management Division Program Review held in May 1992 in Washington, DC.

Appendix 1

Comparison of Urethane Topcoat Requirements

Specification	MIL-C-83286B	MIL-C-85285B	BMS 10-60H
<i>General</i>	low solids VOC 560-650 g/l	high solids VOC <420 g/l	
Toxicity	free isocyanate < 1.0%, aliphatic isocyanates only	free isocyanates < 1.0% No Pb <i>ASTM D 3432 & D 3335</i>	material shall be health safe curing mixing, application, and cure.
Volatile Content	min % solids from 35 to 52% depending on color <i>FTMS 141 no. 4041.1</i> <i>ASTM D 126</i>	Type I < 420 g/l Type II < 350 g/l no halogenated solvents <i>ASTM D 3960</i>	± 2% on non-volatile content <i>ASTM D 2369 & D 1353</i>
<i>Component Properties</i>			
Condition in Container	homogeneous, free from lumps, thickening, or gelatinization <i>FTMS 141 no. 3011.1</i>	homogeneous, free from lumps, thickening, or gelatinization	no caking, free from skins, livering, gelled particles when viewed on glass plate <i>FED-STD 141 no. 3011.1</i>
Storage Stability	stable for 1 year	stable for 1 year	stable for 1 year
Moisture Content	<1.75% <i>FTMS 141 no. 4081</i>	<1% <i>ASTM D 1364</i>	
<i>Liquid Properties</i>			
Fineness of Grind	gloss min. 7, camouflage min 5 on Hegman scale 1 hr after mixing <i>FTMS 141 no. 4411.1</i>	gloss min. 7, camouflage min 5 on Hegman scale 1 hr after mixing <i>ASTM D 1210</i>	
Coarse Particles		<0.5% by wt retained on no. 325 sieve <i>ASTM D 185</i>	
Odor	not obnoxious <i>FTMS 141 no. 4401</i>	no residual odor after 48 hrs, wet or dry coating not obnoxious	

Appendix 1 (Continued)

Viscosity	17 to 23 sec through no. 2 Zahn cup, with exceptions and aged 6 hr test <i>ASTM D 562</i>	<30 sec through no. 4 Ford cup at maximum VOC content <i>ASTM D 1200</i>	± 20% of value provided by the supplier
Pot Life	6 hrs, up to 20% thinner may be added, viscosity increase < 6 sec	viscosity <60 sec through no. 4 Ford cup after 4 hrs in closed container, no gel in 8 hrs <i>ASTM D 1200</i>	meet all specs at 4 hr (white), 3 hrs (other colors), or 1 hr (metallics) after mixing
Weight per Gallon			± 0.25 lb from label . <i>ASTM D 1475</i>
<i>Film Properties</i>			
Drying Time	dry to recoat in 1 hr. set to touch in 2 hrs. dry-hard in 7 hrs. <i>FTMS 141 no. 4061.1</i>	set to touch in 3 hrs. dry-hard in 8 hrs. <i>ASTM D 1640</i>	
Surface Appearance	smooth, uniform, free from bubbles, pinholes, holidays, or other irregularities	uniform, smooth surface when sprayed initially or 4 hrs after mixing	good spraying properties at 8 to 10 inches <i>FED STD 141 no. 4331.1</i>
Color	match FED-STD-595 color chip after 24 hrs drying time	match FED-STD-595 color chip after 24 hrs drying time	match applicable Boeing or FED-STD 595 color standard
Infrared Reflectance		specified for aircraft grey only	
Gloss	at 60° incidence: gloss colors min 90, camouflage max 7 <i>FTMS 141 no. 6101</i>	at 60° incidence: gloss colors min 90; semi-gloss min 15, max 45; camouflage max 3 <i>ASTM D 523</i>	at 60° incidence: initial - gloss min 90; semi-gloss 20-40; flat max 5; at pot life - gloss min 87; semi-gloss 20-40; flat max 5
Hiding Power	contrast ratio min 0.85 to 0.95 depending on color <i>ASTM D 1738</i>	contrast ratio min 0.9 <i>ASTM D 2805</i>	at 2.4 mil thickness - contrast ratio 0.95 light colors, 1.00 dark colors
Pencil Hardness			HB min, some require 2B min

Appendix 1 (Continued)

Adhesion	wet tape test <i>FTMS 141 no. 6301.1</i>	after water immersion, will not peel in tape test, scrap test w/3 kg weight <i>FED STD-141 no. 6301</i> <i>ASTM D 2197</i>	
Flexibility - Impact	impact flexibility after 24" drop of test mandrel	min impact elongation Type I 40%, Type II 10%	no cracking, flaking, or loss of adhesion when forward or reverse impact of 40 in. lbs.
Flexibility - Cold Bending	-65°F, gloss 1" mandrel, camouflage 2" mandrel <i>FTMS 141 no. 6222 & 6226</i>	-60°F, Type I gloss/semi-gloss 1" mandrel, camouflage 2" mandrel, Type II no test	-65°F, 4" mandrel test after 24 cycles of 160°F (25 min) and -65°F (5 min), Type I or II.
<i>Resistance Properties</i>			
Fluid Resistance	allowed 1 (2 for Skydrol) pencil hardness decrease <i>FTMS 141 no. 6011</i>		no blistering, softening, cracking, or peeling after exposure @ 75°C
	24 hrs in lub oil @ 121°C	24 hrs in MIL-L-23699 lub oil at 121°C	14 days in MIL-L-7808 oil
	7 days in MIL-H-5606 hydraulic fluid @ 25°C	24 hrs in MIL-H-83282 hydraulic fluid at 66°C	14 days in MIL-H-5606 hydraulic fluid
	7 days in Skydrol 500B @ 25°C		30 days in BMS 3-11 hydraulic fluid, min pencil hardness of B on dry film
	4 days in distilled water @ 100°F		7 days in distilled water, no blisters larger than #8 per <i>ASTM D 714</i>
	7 days in TT-S-735 Type III fluid @ 25°C		14 days in TT-S-735 Type III fluid

Appendix 1 (Continued)

Weather Resistance	500 hrs carbon arc 1 yr outdoor in FL, 10% loss in gloss permitted <i>FTMS 141 no. 6152</i>	500 hrs Xe weatherometer 1 yr Key West, FL, gloss at 60° gloss min 80, semi-gloss min 15, camouflage max 3	gloss retention > 70 after 500 hrs artificial weathering, >60 after 300 hrs in Atlas UVCON weathering device; free film tensile of 2000-6000 psi and min 50% elongation after 2000 hrs artificial weathering
Humidity Resistance	30 days @ 95% RH & 120°F <i>FTMS 141 no. 6201</i>	30 days @ 100% RH & 120°F <i>ASTM D 2247</i>	
Heat Resistance	4 hrs @ 300°F <i>FTMS 141 no. 6051</i>	1 hr @ 250°F <i>FED STD-141 no. 6051</i>	
Solvent Resistance		rub with MEK soaked rag	
Tape Resistance	no marring by masking tape after 6, 7, or 16 hrs depending on color	no marring by masking tape after 8 hrs of air dry	no staining & only slight visible mark after 6 hrs of drying in oven at 90°F
Salt Spray Resistance	500 hrs in 5% salt spray with no visible corrosion <i>FTMS 141 no. 6061</i> <i>ASTM B 117</i>		no corrosion extending > 1/8 in beyond scribe mark after 3000 hrs exposure to salt spray fog
Electrical Resistance			0.07 megohm min.
<i>Working Properties</i>			
Cleanability		90% min cleaning efficiency	
Strippability		90% stripped in 60 min with MIL-R-81294 paint remover	

Appendix 2

Screening Tests for Urethane/Acrylate Topcoats

The procedure laid out in the Phase III DoE proposal calls for an initial set of screening tests (as part of sub-task 1.2), designed to allow selection of 3 to 5 formulations for further testing, followed by an additional set of qualification tests (as part of sub-task 1.3).

Screening Tests for Sub-task 1.2

Specification	Criterion	Test Method	Reference Specification
60° Gloss	minimum 90	ASTM D 523	BMS 10-60 para 8.2.5
Adhesion	Wet tape test	FTMS 141 - 6310.1	MIL-C-83286 para 3.7.2.1
Flexibility - Impact	no cracking, crazing or removal of coating by tape test after 24 inches mandrel drop or 40 inch pounds	FTMS 141 - 6226	MIL-C-83286 para 3.7.2.2 BMS 10-60 para 8.2.12
Flexibility - Cold Bending	-35°C, no cracking or crazing with 1" mandrel bend	FTMS 141 - 6222 ASTM D 1737 (?)	MIL-C-83286 para 3.7.3.4
Skydrol Resistance	decrease of less than 2 pencil hardness after 7 days @ 25°C	FTMS 141 - 6011 BSS 7263	MIL-C-83286 para 3.7.3.5
Distilled Water Resistance	decrease of less than 1 pencil hardness after 7 days @ 25°C	FTMS 141 - 6011	MIL-C-83286 para 3.7.3.5
Salt Spray Resistance	no corrosion after 500 hrs in 5% salt spray	ASTM B 117	MIL-C-83286 para 3.7.3.1

Appendix 2 (Continued)

Additional tests for Sub-task 1.3 (performed on 3-5 formulations)

Specification	Criterion	Test Method	Reference Specification
Pot Life	meet all specs at 4 hrs (white) or 3 hrs (colors)		BMS 10-60 para 8.2.2
Skydrol (BMS 3-11 fluid) Resistance	minimum pencil hardness of B for dry film, after 30 days @ 25°C		BMS 10-60 para 8.2.13
Weather Resistance	gloss retention > 70 after 500 hrs artificial weathering, >60 after 300 hrs in Atlas UVCON weathering device; free film tensile of 2000-6000 psi and min 50% elongation after 2000 hrs artificial weathering		BMS 10-60 para 8.2.14
Humidity Resistance	no loss of adhesion, blistering, or softening after 30 days @ 95% RH and 120°F	FTMS 141 - 6201	MIL-C-83286 para 3.7.3.2
Heat Resistance	must pass gloss and impact flexibility after 4 hrs @ 300°F	FTMS 141 - 6051	MIL-C-83286 para 3.7.3.3
Cleanability	90% cleaning efficiency		MIL-C-85285 para 3.9.3
Strippability	90% stripped in 60 min with MIL-R-91294 paint remover		MIL-C-85285 para 3.9.4

Appendix 3

Comparison of Epoxy Primer Requirements

Specification	MIL-P-23377F	MIL-P-85582A	BMS 10-79K
<i>General</i>	Class 1 - Standard Solvents Class 2 - High Solids Class 3 - Exempt Solvents	Epoxy, Waterborne bisphenol-A-type Epoxy Cl 1 - Ba chromate Cl 2 - Sr chromate	Corrosion Resistant Primer Gr A - Conventional Solvents Gr B - Low VOC/Exempt Solvent Gr C - Low VOC/Conv. Solvent Type II Urethane compatible Type III <1% aromatic amine
Toxicity	No lead permitted <i>ASTM D 3335</i>		
Chromate Content (in component A)	Type I min 52% of pigment weight, Type II min 42%, must be strontium chromate.	Type I & II: CrO ₃ min 15.7% of pigment weight Type I TiO ₂ min 13.0%	
Pigment Content	Component A contains min % solids: Cl 1 & 2 - 37%, Cl 3 - 35%	min 45% of solids in admixed primer <i>FTMS 141 no. 4021</i>	
Volatile Content	Cl 2 & 3 <340 g/L <i>ASTM D 3960</i>	<340 g/L; chlorinated solvents not permitted	Gr A: apx 650 g/L Gr B & C: < 350 g/L
<i>Component Properties</i>			
Condition in Container	homogeneous, free from lumps, thickening, or gelatinization <i>FTMS 141 no. 3011.1</i>	homogeneous, free from lumps, thickening, or gelatinization <i>FTMS 141 no. 3011.1</i>	homogeneous, free from lumps, thickening, or gelatinization <i>FTMS 141 no. 3011.1</i>
Thinner	Cl 1 & 2 - compatible with any MIL-T-81772, type II thinner, Cl 3 - compatible with 1,1,1-trichloroethane	water, must meet type IV requirements of ASTM D 1193	

Appendix 3 (Continued)

Fineness of Grind	min 5 on Hegman scale <i>ASTM D 1210</i>	min 5 on Hegman scale <i>ASTM D 1210</i>	min 5 on Hegman scale <i>ASTM D 1210</i>
<i>Liquid Properties</i>			
Storage Stability	stable for 1 year <i>FTMS 141 no. 3022</i>		Grade A 12 mo, Gr B 9 mo, Gr C 6 mo.
Accelerated Storage Stability	stable for 7 days @ 60°C <i>FTMS 141 no. 3019</i>	stable for 7 days @ 49°C <i>FTMS 141 no. 3019</i>	
Freeze thaw Stability		meet all requirements after 5 freeze thaw cycles <i>ASTM D 2243</i>	
Color	Type I - deep yellow Type II - dark green	Type I - light green Type II - dark green	
Odor	not obnoxious <i>ASTM D 1296</i>	not obnoxious <i>ASTM D 1296</i>	no discomfort to operator
Viscosity	Cl 1 & 3: 22 sec through no. 4 Ford cup; Cl 2: 40 sec through no. 4 Ford cup <i>ASTM D 1200</i>	solids > 20% when thinned to 14 sec through no. 4 Ford cup <i>ASTM D 1200</i>	Grade A: 35 ± 5 sec no. 1 Zahn cup, Grade B: 12-16 sec no. 2 Zahn cup, Grade C: 3500-9500 cps @ 20 rpm no. 4 spindle in Brookfield Viscometer
Pot Life	Cl 1 & 3 <30 sec through no. 4 Ford cup after 8 hrs; Cl 2 < 70 sec through no. 4 Ford cup after 4 hrs	when initially thinned to 14 sec & constantly stirred @ 140 rpm, < 22 sec through no. 4 Ford cup after 4 hrs	Grade A: 8 hrs, Gr B 6 hrs, Gr C 3 hrs
Total Solids	admixed primer Cl 1 - 42%, Cl 2 - 65%, Cl 3 - 38% min by weight <i>ASTM D 2369</i>	admixed primer 40% min by weight <i>ASTM D 2369</i>	
<i>Film Properties</i>			
Drying Time	Cl 1 & 3: tack-free in 1 hr, dry-hard in 6 hrs. Cl 2: tack-free in 5 hrs, dry- hard in 8 hrs <i>ASTM D 1640</i>	tack-free in 1 hr, dry-hard in 6 hrs. <i>ASTM D 1640</i>	dust free 30 min, tape masking 2 hrs, overcoating w/o loss of adhesion 2 hrs.

Appendix 3 (Continued)

60° Gloss		Primer only, max 10 units @ 24 hrs, Primer & Topcoat, min 90 <i>ASTM D 523</i>	
Surface Appearance	no sagging, running or streaking, free from grit, seeds, craters, blisters, or other irregularities	no sagging, running or streaking, free from grit, seeds, craters, blisters, or other irregularities	
Infrared Reflectance	Type II only <10% in range 450 to 2700 nm	Type II only <10% in range 450 to 2700 nm	
Lifting	no evidence of lifting upon applying a polyurethane topcoat after 5 hr air dry	no evidence of lifting upon applying a polyurethane topcoat after 2, 4, & 18 hr air dry	
Solvent Retention	CI 3: retain <1% of original solvent @ 7 day, room temp. cure <i>ASTM F 151</i>		
Strippability	90% removal in 60 min @ room temp with MIL-R- 81294, type I, CI 1 paint remover	90% removal in 15 min @ room temp with MIL-R- 81294 paint remover	
Dry Adhesion		Parallel groove adhesion of not less than 4 microknife adhesion units <i>ASTM D 2197 Method B</i>	No removal with dry tape peel
Wet Adhesion	24 hr immersion in water <i>FTMS 141 no. 6301.1</i>	24 hr immersion in water <i>FTMS 141 no. 6301.1</i>	7 day immersion in water, no removal with tape peel
Flexibility - Impact	min impact elongation 10%	min impact elongation 10%	Grades A & B only: no cracking @ 40 in-lbs.
Flexibility - Bending			Grades A & B only: 180° conical bend <i>ASTM D 522</i>

Appendix 3 (Continued)

Flexibility - Low Temperature Shock			24 cycles: 160 to -65°F, 4 in mandrel bend at -65°F
Pencil Hardness			min H BSS 7263
Compatibility with Epoxy Primers			shall adhere to BMS 10-11 type I and BMS 10-20 type II
Compatibility with Urethane Topcoats			All BMS 10-60 type II materials meet adhesion, hydraulic fluid resistance, and corrosion tests
<i>Resistance Properties</i>			
Fluid Resistance	when topcoated, 4 days in distilled water @ 120°F	when topcoated, 4 days in distilled water @ 120°F	
	24 hrs in lub oil @ 121°C	24 hrs in lub oil @ 121°C	
	24 hrs in MIL-H-83282 hydraulic fluid @ 66°C	24 hrs in MIL-H-83282 hydraulic fluid @ 66°C	30 days in BMS 3-11, Grades A&C no softer than HB, Gr B no softer than 4B
Solvent Resistance	rub with MEK soaked rag back and forth 25 times	rub with MEK soaked rag back and forth 25 times	
Rain Erosion Resistance			primer and topcoated system peels less than 1/4 inch during 30 min test
Salt Spray Resistance	1000 hrs in 5% salt spray with no visible corrosion on Al, 500 hrs on graphite/epoxy FTMS 141 no. 6061 ASTM B 117	1000 hrs in 5% salt spray with no visible corrosion on Al, 500 hrs on graphite/epoxy FTMS 141 no. 6061 ASTM B 117	Type II primer, 500 hrs Type II primer + topcoat or Type III primer, 3000 hrs 5% salt spray
Filiform Test	1 hr in desiccator with 12N HCl, 1000 hrs @ 104°F and 80% humidity, panel primed and topcoated ASTM D 2803	1 hr in desiccator with 12N HCl, 1000 hrs @ 104°F and 80% humidity, panel primed and topcoated ASTM D 2803	1 hr in desiccator with 12N HCl, 30 days @ 104°F and 80% humidity, panel primed and topcoated

Appendix 3 (Continued)

Electrical Resistance			0.06 Mohm-cms min
<i>Working Properties</i>			
Mixing	blend to smooth homogeneous product	blend to smooth homogeneous product	
Dilution	no incompatibility with thinner, does not separate into visually distinct layer after standing 1 hr.	no incompatibility with thinner, does not separate into visually distinct layer after standing 1 hr.	
Application	smooth uniform film with no runs or sags at 0.6 to 0.9 mil dry thickness		smooth uniform film with no runs or sags at 0.6 to 0.9 mil dry thickness